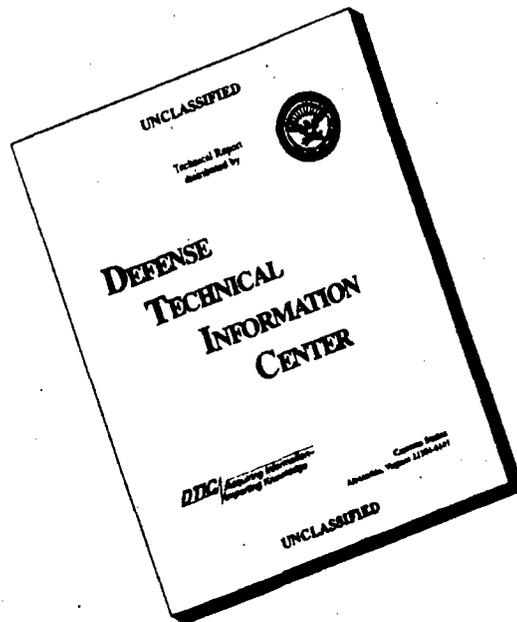


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ABSTRACT

A bibliography of publications dealing with the inorganic chemical composition of ocean water is presented. By a review of this literature several generalizations about the chemistry of ocean water are noted. These facts are used as a standard to compare several existing formulas for synthetic substitutes now in widespread use. Certain faults are revealed in these substitutes.

A new formula is proposed, giving exact reproduction of ion concentrations which are existent in natural ocean water. Provision is made for addition of heavy metal ions when desired. A few experiments conducted with this solution yield results which duplicate similar experiments conducted in natural ocean water.

The solution is recommended for use where spray conditions or high velocity impingement attack may occur. It is not proposed as a substitute for natural ocean water in conditions where biofouling may be an important factor.

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INTRODUCTION

A. Authorization

1. This survey has been made in connection with corrosion studies conducted under the authority for several investigations at this laboratory, namely: Bureau of Ships Project Order Nos. 407/45, 407/46 and 376/44, Bureau of Aeronautics Project Order Nos. 111/43 and 176/44, and Bureau of Ordnance Project Order No. E-4795.

B. Statement of the Problem

2. During the prosecution of investigations mentioned in paragraph (1), it became desirable to conduct some experiments at this laboratory in synthetic ocean water. A preliminary examination of existing formulas revealed serious discrepancies between them and no basis for correcting these discrepancies was apparent. Therefore, a literature search was made to establish as nearly as possible just what various analyses of ocean water have revealed.

3. In the selection of components and the establishment of a standard formulation for a synthetic ocean water, it must be borne in mind that the natural water is a solution of solids and gases which also contains detritus and live marine organisms, both plant and animal. For the purposes of studies other than abrasion and fouling, the suspended matter is of little consequence. The only important gases are oxygen and carbon dioxide; the concentrations of these is determined by the chemical composition of dissolved solids, the total salinity, temperature and the partial pressures of the gases in the atmosphere. Their presence needs control during the course of experiments and is not therefore discussed in this report. Furthermore, it must be realized that an exact correlation with actual ocean water will not be possible under conditions of mild and negligible turbulence because in natural ocean waters marine organisms become attached to surfaces and thence influence corrosion processes. Under conditions of high turbulence, it is quite probable that organic matter plays a minor role in corrosion processes. The only suitable control in preparing a synthetic ocean water is that of the chemical composition. Considerations of the chemical composition revolve about the selection of ions, which are important in corrosion processes, and of the concentrations of these ions.

DISCUSSION

A. Existing formulas for Synthetic Ocean Water

4. Laboratory pre-service tests for determining corrosion characteristics have been extensively used for many years. In testing items of interest to the Navy, it is often desirable to study their behavior in ocean water. However, the use of actual ocean water is seriously limited by its availability, especially to inland laboratories, and it suffers

an additional disadvantage in that samples drawn at different places may have varying compositions. Sea salt has been extensively used but it too does not have a constant composition if the salt is obtained from water near the shore. Because of these difficulties in obtaining a natural ocean water of constant composition, a number of more or less arbitrary formulations for artificial ocean water have been improvised. In some instances, these formulations have been established by purely arbitrary means and were intended for specific applications; they are not always suitable for general application. In other instances, these formulations are not even close approximations of the average composition of mid-ocean waters.

5. For the corrosion testing of certain steels, Bureau of Ships ad interim specification 46Sl8e prescribes the formula given in Table I. The formula in Table II is specified in Bureau of Ships ad interim specification 14-0-15 for testing noncorrosive, turbine lubricating oils.

6. At this laboratory the composition given in Table III has been used quite extensively. The formula given in Table IV has actually been used in some laboratories but it obviously is not very satisfactory because of the listing of iron and aluminum as insoluble oxides. Another formulation in Table V, proposed by McClendon, Gault, and Mullholland (26), has been used to study certain marine organisms; it contains nitrate, phosphate, and silicates which are essential in the metabolism of the organisms. In corrosion studies, it is doubtful if the compounds below the concentration of boric acid are essential. Formulas containing only the major constituents have been used by Subow (108) and by Lyman and Fleming (8); these are listed in Tables VI and VII.

7. These formulas and others used by various groups have been applied to the same problems and, as a result, discrepancies have arisen among reports on ocean water tests of various materials. Such discrepancies serve to indicate the advisability of standardizing all studies in synthetic ocean water by the use of water with a single composition.

B. Investigations of the Chemical Composition of Ocean Water

8. Considerable effort has been devoted to analyses of ocean water by many investigators. A few have considered the concentrations of many ions but more frequently each investigator has reported on only one or a few ions. The reasons for this become obvious when one considers the complexity of ocean water and the difficulties of the analytical methods. For the purposes of this report, a detailed account of all these results would add little and requires too much space for inclusion here. In particular instances where more information is desired, the investigator is referred to the bibliography at the end of this report. Numbers 1 through 30, inclusive, refer to general discussions and complete analyses.

11. The determination of salinity is difficult and slow with the result that it is rarely carried out. By titration with silver nitrate using potassium chromate as an indicator, total halides can be more readily determined. The resultant value, reported in grams per kilogram, is called chlorinity. More exactly, it is now defined as the weight of silver required to completely precipitate the halogens in 0.3285233 kilogram of ocean water. This value is based upon a so-called "normal ocean water" sample prepared in 1937 by Jacobsen and Knudsen (90) which is distributed as a standard for oceanographic studies by the Hydrographical Laboratories in Copenhagen, Denmark. Chlorinity is related to salinity according to the equation

$$\text{Salinity} = 0.03 + 1.805 \times \text{Chlorinity}$$

12. The explanation for the first generalization of paragraph (9) is self-evident. The total salt concentration in river waters is very low. These waters are also comparatively rich in calcium and sulfate ions, a fact which frequently alters the relative proportions of these ions.

13. The second generalization is not surprising but does require further explanation. The salt content of the open oceans normally lies between the extremes of 3.3 and 3.8%. Wüst (154) showed the overall average for ocean surface salinity to be 35.11 grams per kilogram of ocean water. At any particular position other values may exist. From a low 3.3% in the Aleutian region, the surface salinity of the Pacific Ocean during the northern summer rises to a maximum of about 3.55% in the mid-north Pacific and falls to about 3.45% at the Equator. In the southern hemisphere, it rises to greater than 3.65% in mid-south Pacific and drops off to 3.35% at the Antarctic. The Indian Ocean varies according to Schott (124) from 34.5 salinity in the north through a maximum of slightly over 36.0 west of Australia to 33.5 at the Antarctic. The Atlantic exhibits slightly higher salinities (7). From a low of 34 south of Greenland it rises to a maximum of 37 midway between the West African Shore and the West Indies. Further South, this decreases to about 35 between Brazil and West Africa, rises again to 37 off the southeast coast of Brazil and decreases to 34 at the Antarctic border. These values will vary somewhat from time to time.

14. Changes in the salt content in respect to position, depth and time, are the result of currents, wave motion and turbulence as well as evaporation and precipitation. In the temperate zones, the precipitation and evaporation are moderate. In tropical regions, high humidity results in moderate evaporation while in polar regions, where evaporation is low, the precipitation is relatively large. Wüst (154), in studies of the Atlantic, Pacific and Indian Oceans, showed the salinity to be a linear function of the difference between evaporation (E) and precipitation (P).

$$S = 34.60 + 0.0175 (E-P) \quad 14.1$$

Figure 1, an approximate reproduction of Wust's data for the average surface salinity of all oceans at a given time, demonstrates the variation of salinity with latitude. Since the difference between evaporation and precipitation changes with the time of year, the salinity at a given position also changes. Figure 2 from Bohmecke's data on the North Atlantic area in 1938 shows how the salinity varies with the month in this region (42). No data is available in regard to diurnal variations in salinity but it is probable that they are small.

15. Because of incomplete mixing, the salinity at a given time and position will vary with depth. As an example, the surface salinity of the mid-Pacific Ocean at the equator according to Mears (13) is at a particular time about 36.5 while at 1000 meters it was 34.7. Vertical mixing of the surface waters with this lower stratum, which exists at 600-1000 meters below the surface, has a considerable control over the surface salinity.

16. The analytical determinations of most ions in ocean water involve difficult procedures because of the large number of ions in the ocean and the wide range of concentrations encountered. Whereas sodium and chloride ions are present in high concentrations, other ions such as fluoride and borate occur in ocean water in only small amounts. Then, too, many ions are so nearly alike the determination of each one becomes quite a task; for example, like groups of elements which cause this difficulty are sodium and potassium, calcium and strontium, and chloride, bromide and iodide. The analytical procedures are not discussed in this report; the procedures for the more common ions are discussed by Harvey (7) and the others can be reviewed by direct reference to papers in the bibliography. It suffices to say here that the most probable values have been selected from these papers.

17. Table VIII presents a list of the elements other than hydrogen and oxygen in ocean water as compiled by Sverdrup, Johnson and Fleming (25). Column (2) gives the concentration in mg. per kg. of solution corresponding to a chlorinity of 19.00 grams per kilogram of ocean water. Column (3) indicates by reference number the source of the values reported. The value for nitrogen does not include the inert, gaseous element which is dissolved to a very slight extent. The concentrations given for silicon and some of those elements below fluorine may vary because of local conditions such as above-average marine growth. Of the major components, i.e., those present in amounts above 1 p.p.m., the relative proportions remain constant in mid-ocean waters regardless of the salinity. Table IX lists the ions in which these major elements appear in ocean water according to Lyman and Fleming (11). Column (1) names the ion, column (4) gives the concentration in grams per liter corresponding to a chlorinity of 19.381. Column (2) lists the Cl-ratio for these ions while in column (3) is listed the probable uncertainty of these ratios. Column (5) gives the source by number reference to the bibliography. The Cl-ratio factors are ratios for each ion based on

chlorinity and chlorosity (chlorosity is the volumetric term equivalent to chlorinity, that is,

$$\text{Chlorosity} = \text{Chlorinity} \times \text{Density at } 20^{\circ}\text{C.}$$

These ratios were first established by Dittmar (4) from 77 samples collected during the voyage of H.M.S. Challenger in 1884. They were brought up to date in 1940 by Lyman and Fleming (11). The more recent value for bromide reported by Thompson and Korpi (133) is slightly higher than Lyman and Fleming's value but has not been used. The difference amounts to 1.5 mg. of bromide ion per liter and is not considered to be serious.

D. Comparison of Synthetic Ocean Waters With Natural Ocean Waters.

18. In Table X, the compositions of the various synthetic ocean waters and natural ocean water are compared by their ion concentration, calculated from Table I - VII, inclusive, and by their chlorinities. The ion concentrations in natural ocean water with chlorinities of 19.0 and 19.381 are shown respectively in Columns (2) and (3). The values for two chlorinities are given to facilitate comparison of the synthetic solutions. These values are used to calculate the Cl-ratios in Table XI. The data in Column (4) of Table X and Column (3) of Table XI are calculated from a formula to be discussed later. Among the other formulas, it is to be noted that Lyman and Fleming's, Subow's, and McClendon's are adjusted to a chlorinity of 19.00 which is about 0.38 grams per kilogram of ocean water lower than the average value for natural ocean water; however, this value is within the range of variations actually observed. Comparison with the data in Column (1) of these tables shows only minor deviations in the ion concentrations and Cl-ratios for Lyman and Fleming's formula. The deviations are slightly larger for Subow's formula which is also lacking boric acid and fluoride ion. The formula of McClendon et al shows much greater deviations and also contains some compounds which are probably not important in many corrosion studies.

19. The last four columns of these Tables contain data from formulas in more or less common use by the Navy. Only the one in specification 14-0-15 has a suitable chlorinity, but these formulas have far more serious faults. None of them contain bicarbonate ion which is necessary to maintain a suitable pH. The Cl-ratio for Mg^{++} is 10% higher in 46S18 formula and 30% low in Navy Standard formula. The Cl-ratio for K^{+} is only 5% of what it should be in the NRL Report P-1381. Sulphate ion is 5% low in 46S18; bromide ion is tenfold too high in this formula. In P-1381 and Navy Standard, bromide is 40% too low. In P-1381, iodide is 80 times the normal value and in Navy Standard 800 times. Lesser faults in these specification formulas are the absence of fluoride and boric acid.

E. Proposal of a Formula to Serve as a Standard Composition

20. The need for comparison of test results between different laboratories and hence the need for standardization of test methods of test

solutions is self-evident. One must, however, before choosing a standard ocean water solution give some attention to the possible uses to which the water may be put. This is necessary in order to set rational limits for the accuracy of the ocean water composition. For fundamental research on the corrosion of metals and for research on the physical properties of ocean water, the composition of the solution should equal the accuracy with which the original determination was made. For research testing of materials, a formula accurate to 0.1% should be satisfactory. For routine testing in accelerated spray or immersion tests, accuracy of 1.0% for each constituent is probably sufficient.

21. In Table XII is proposed a formula which reproduces the ion abundance of ocean water with a chlorinity of 19.381; these values are given to the accuracy with which they are known. On referring to Table VIII, it is noted that this formula disregards elements below fluorine. This admittedly is arbitrary and is done to simplify preparation of the solution. Fluorine is included since it is normally present to a degree sufficient to effect the chlorinity within the accuracy now obtainable. In routine testing, omission of fluoride may not be a serious matter. In some corrosion studies where the heavy metal salts are considered desirable, it is suggested that they be added as their nitrates in accordance with the chlorinity being used and the concentrations expressed in Table VIII. Column (2) of Table XII gives a formulation which reproduces the known concentrations with greatest accuracy. These values may be rounded off where such accuracy is not warranted. Column (3) suggests a composition which is more readily prepared and is satisfactory for test procedures.

22. The salts listed in Table XII were chosen for their ease in handling and their availability in a pure state. Sodium chloride, potassium chloride, potassium bromide, sodium bicarbonate and sodium fluoride may be dried easily and accurately weighed. Sodium sulfate and calcium chloride tend to pick up moisture during the weighing process and for that reason require special care. Magnesium and strontium chlorides are available in a pure form but the degree of hydration of each is uncertain. Fortunately the strontium chloride is present in such small quantities in ocean water that no appreciable error is introduced if the reagent grade salt is weighed directly. Magnesium chloride, however, must be weighed to 11 mg. for Class II work and to 0.2 mg. for Class I work. This calls for salt purity of 99.9% and 99.99% respectively and such purity may only be obtained by carefully drying the material.

23. In preparing this solution for fundamental research (Class I), sodium chloride and sodium sulfate should be reprecipitated from aqueous solutions and dried in an oven at 500°C. The magnesium chloride must be moistened and dried in a desiccator over 80% sulfuric acid. Pure calcium chloride may be prepared by passing dry HCl gas over the reagent grade of material at 600°C. The remaining salts are present in sufficiently small quantities that reagent grade chemicals may be used directly without further purification. For less exacting studies, sodium chloride

sodium sulfate and calcium chloride may be dried simply in an oven at 130°C. The degree of hydration of magnesium chloride must be regulated as above while all other components may be used as reagent grade without further purification. Distilled water should be used in all preparations.

24. It has been found convenient and more accurate to prepare two stock solutions; one containing the hygroscopic salts, magnesium chloride, calcium chloride and strontium chloride, the other containing sodium fluoride, potassium bromide, sodium bicarbonate and potassium chloride. Stock solution No. 1, containing the hygroscopic salts, is made up to a concentration 350 times that listed in Table XII; stock solution No. 2 is 700 times as concentrated. The synthetic ocean water is then prepared by mixing these solutions with sodium chloride and sodium sulfate followed by dilution as indicated in Table XIII. It will be found that the solution at this point has a pH of 7.5 to 7.8, dependent upon the carbon dioxide concentration in the distilled water. Since this is lower than the average value of natural ocean water (pH = 8.2), it is necessary to add 0.1 n. sodium carbonate solution to raise this to 8.2. This procedure will raise the Cl-ratio for bicarbonate ion slightly but, if good chemicals and water are used, this will not exceed 5-10%; the effect on the Cl-ratio for sodium ion will be less than 1%. It is more important to adjust the pH than to maintain rigidly the Cl-ratios for these ions.

25. When a synthetic ocean water containing heavy metal ions is desired, the solution is prepared according to Table XIII; the stock solution in Table XIV is used to add the heavy metal ions. Any of these ions may be omitted or others not listed may be added as desired. Since the chlorides of silver and lead are not very soluble, the addition of this stock solution is best made to a large bulk of distilled water, e.g., one or two liters, being used to prepare the solution with Stock Solutions Nos. 1 and 2. If Stock Solution No. 3 is added to the 10 liters of synthetic ocean water, this addition should be slow and with vigorous agitation to reduce the possibility of precipitating silver or lead. Use of this solution will bring these heavy metals up to the concentrations required for a chlorinity of 19.381 and correspond to the values in Table VIII for a chlorinity of 19.00. The nitrate concentration introduced by this stock solution will be 0.104 mg. per liter, well within the limits indicated in Table VIII.

SOME RESULTS OBTAINED BY THE USE OF THE PROPOSED FORMULA

26. During investigation of the anodic behavior of zinc, an opportunity was presented for comparing the corrosion products formed in this synthetic ocean water with those formed in natural ocean water on zinc anodes attached to the hull of the U.S.S. Forrest. With a number of zinc alloys, it was immediately evident that the corrosion products in the two media were as identical as reproducibility among a number of specimens in the same medium permitted. The texture of the products was identical; a

metallic gray deposit was found next to the metal and was covered in both instances by a gray-white deposit. Examination by x-ray diffraction showed the same crystal structure in natural and synthetic waters. Table XV compares such products by using data extracted from NRL Report No. P-2592; Columns (1) and (2) list the interatomic distances calculated from the diffraction patterns of zinc corrosion products. Columns (3), (5), and (6) show the interatomic distances for known preparations of basic zinc carbonate and basic zinc sulfates. Column (4) gives values for basic zinc chloride, Column (7) for zinc hydroxide. These data made it immediately apparent that the corrosion of zinc in ocean water leads to the formation of chiefly basic zinc carbonate and sulfate. It is obvious therefore that the selection of a synthetic solution must provide the proper concentrations of bicarbonate and sulfate ions as well as correct pH.

27. Although laboratory experiments on cathodic behavior of steel in synthetic ocean water have been limited, they served to check semi-quantitatively the results obtained on a larger scale in natural ocean water at Kure Beach, N.C. They also serve to illustrate important differences between the cathodic behavior of steel in sodium chloride solution and in ocean water. At cathodic surfaces in sodium chloride solution, polarization occurs because of a concentration gradient in the solution next to the electrode surface and accumulation of soluble alkali at the surface. In ocean water this same phenomena occurs but it augmented by the precipitation of alkaline earth metals as their insoluble carbonates (chiefly aragonite or calcium carbonate at low current densities). As a result much less current is required to protect steel in the presence of bicarbonate and calcium ions than in their absence. For this reason, results obtained with sodium chloride solutions are not comparable directly to what occurs in natural ocean waters when couples of dissimilar metals are under consideration.

28. A few experiments were conducted to compare the corrosion rates of a low carbon, mild steel in fogs of 0-20% sodium chloride solution and of the synthetic ocean water. Runs were made at 95°F under conditions which conformed with the Federal Specifications QQ-M-151 except when concentrations were deliberately changed; specimens were 1/32" x 3" x 4", sandblasted on one side and painted on the other. The unpainted side was placed upward at an angle of 75° with the horizontal and exposed for 24 hours. After cleaning and removing paint, the weight losses were determined. Table XVI shows the 24-hour corrosion rate in sodium chloride spray. The 24-hour weight loss for the synthetic ocean water was 3.59 mg. per sq. dm. which compares with 10% sodium chloride spray. Other metals could not be compared in the same manner without obtaining weight losses in the two exposures for the specific metals.

CONCLUSIONS

29. It is concluded that synthetic ocean waters now existent in Navy Specifications are not representative of natural ocean water; it is further concluded that a suitable representative solution can be prepared as described in Tables XIII and XIV.
30. The proposed formula for synthetic ocean water duplicates results obtained in natural ocean water.
31. The proposed formula corrodes unprotected steel at 95°F, when exposed to a fog or spray of this solution, at a rate corresponding to 10% sodium chloride spray. Similar experiments with other metals are necessary to render results in this solution comparable to those obtained in sodium chloride spray.
32. The corrosion of zinc in solutions containing no bicarbonate and sulfate ions cannot duplicate the results obtained in natural ocean water.

RECOMMENDATIONS

33. It is recommended that the formulas for synthetic ocean water now prescribed in Bureau of Ships Specifications 46S18 and 14-0-15 and in other specifications requiring synthetic ocean water be replaced by the more representative formula proposed in this report.
34. It is recommended that laboratories conducting spray tests with sodium chloride solutions, either in routine testing or in support of research and development, plan a program to supplement their test procedures using sodium chloride, use of which is supported by long accumulation of data but is not otherwise justified, with parallel studies using the synthetic ocean water proposed in this report.
35. It is further recommended that this formula be given consideration in the study of impingement attack, or corrosion at high water velocities, of metals and alloys, in the exposure studies of thin film rust preventives and the more durable coatings such as paints, lacquers, enamels and varnishes, and in studies of packaging materials and methods.
36. It is not expected that laboratory use of this solution will duplicate phenomena in natural ocean water under conditions conducive to heavy fouling. The latter condition is known to have a considerable influence on deterioration of protective coatings and corrosion of metals.

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APPENDIX

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76. Greenwald, J. Biol. Chem., <u>141</u> , 789 (1941)	CO ₃
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97. Labbe, Compt. rend. <u>195</u> , 1297 (1932)	pH
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100. McClendon, Gault and Holland, Carnegie Inst. Washington Pub. No. 251, 21 (1917)	CO ₂
101. Mitchell and Rakestraw, Biol. Bull., <u>65</u> , 437 (1933)	NO ₂
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114. Revelle, Dissertation, Univ. of Calif., 1936	pH
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117. Robinson and Knapman, J. Marine Res., <u>4</u> , 142 (1941)	Na
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	<u>Ions</u>
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143. Wattenberg, Internat. Assn. Phys. Oceanogr., Proces-verb., <u>53</u> , No. 7 (1933)	NH ₃
144. Wattenberg, Fortschritte d. Minera., Kristal. u. Petrographie, <u>20</u> , 168 (1936)	CO ₃
145. Wattenberg, Kieler Meeresforschungen, <u>2</u> (1937)	Mg, Sr
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148. Webb, Nature, <u>142</u> , 751 (1938)	Sr
149. Webb, J. Exper. Biol., <u>16</u> , 178 (1939)	Na, K
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TABLE I

SYNTHETIC SEA WATER FOR TESTING STAINLESS STEELS

(Bureau of Ships ad int. Spec. No. 46-S-18)

<u>Salt</u>	<u>Gms. per Liter</u>
NaCl	23.0
MgCl ₂ .6H ₂ O	11.0
Na ₂ SO ₄ .10H ₂ O	8.0
CaCl ₂ .6H ₂ O	2.20
KCl	0.20
KBr	0.90

TABLE II

SYNTHETIC SEA WATER FOR TESTING RUST PREVENTIVE COMPOUNDS

(Bureau of Ships ad. Interim Specification 14-0-15)

<u>Salt</u>	<u>Gms. per Liter</u>
NaCl	25.0
MgCl ₂ .6H ₂ O	11.0
Na ₂ SO ₄	4.0
CaCl ₂	1.2

TABLE III
SYNTHETIC SEA WATER FROM REPORT P-1381
(NRL Sea Water)

<u>Salt</u>	<u>Gms. per Liter</u>
NaCl	24.337
MgCl ₂	2.955
MgSO ₄ ·7H ₂ O	3.870
CaSO ₄ ·2H ₂ O	1.588
KCl	0.676
KBr	0.0630
KI	0.0056

TABLE IV

"Navy Standard" Sea Water

<u>Salt</u>	<u>Gms. per Liter</u>
NaCl	24.3
K ₂ SO ₄	0.83
MgSO ₄	1.315
CaSO ₄	1.256
MgCl ₂	3.405
NaBr	0.0548
NaI	0.0051
SiO ₂	0.0120
Fe ₂ O ₃	0.0188
Al ₂ O ₃	0.0239

TABLE V

McClendon, Gault and Mulholland's
Formula For Synthetic Ocean Water

<u>Salt</u>	<u>Gms. per kg. of Solution</u>
NaCl	26.726
MgCl ₂	2.260
MgSO ₄	3.248
CaCl ₂	1.153
KCl	0.721
NaHCO ₃	0.198
NaBr	0.058
H ₃ BO ₃	0.058
Na ₂ SiO ₃	0.0024
Na ₂ Si ₄ O ₉	0.0015
H ₃ PO ₄	0.0002
AlCl ₃	0.013
NH ₃	0.002
LiNO ₃	0.0013

TABLE VI

Subow's Formula For Synthetic Ocean Water

<u>Salt</u>	<u>Gms. per Liter</u>
NaCl	27.175
MgCl ₂	2.507
MgSO ₄	3.387
CaCl ₂	1.170
KCl	0.743
NaHCO ₃	0.207
MaBr	0.085

TABLE VII

Lyman and Fleming's Formula For Synthetic Ocean Water

<u>Salt</u>	<u>Gms. per Liter</u>
NaCl	23.476
MgCl ₂	4.981
Na ₂ SO ₄	3.917
CaCl ₂	1.102
KCl	0.664
NaHCO ₃	0.192
KBr	0.096
H ₃ BO ₃	0.026
SrCl ₂	0.024
NaF	0.003

TABLE VIII

Concentrations of Elements Present in Natural Sea Water^a

<u>Element</u>	<u>Mg/Kg</u>	<u>Source</u>
Chlorine	18980	4,90
Sodium	10556	117
Magnesium	1272	27
Sulphur ^b	884	132
Calcium	400	27,91
Potassium	380	87,149
Bromine	65	4
Carbon ^c	27.5	76,114, etc.
Strontium	13.3	14 ⁸
Boron ^d	4.6	48,8 ⁸ ,89
Silicon ^e	0.02-4.0	26,57
Fluorine	1.3	135
Nitrogen ^f	0.01-0.70	82,143,109
Aluminum	0.5	80
Rubidium	0.2	73
Lithium	0.1	128
Phosphorus	0.001-0.10	62
Barium	0.05	73
Iodine	0.05	56,112
Arsenic	0.01-0.02	110
Iron	0.002-0.02	58,83,129,130,141
Manganese	0.001-0.01	136
Copper	0.001-0.01	99
Zinc	0.005	37
Lead	0.004	44
Selenium	0.004	74
Cesium	0.002	29
Uranium	0.0015	67
Molybdenum	0.0005	63
Thorium	0.0005	67
Cerium	0.0004	73
Silver	0.0003	79
Vanadium	0.0003	63
Lanthanum	0.0003	73
Yttrium	0.0003	73
Nickel	0.0001	63
Scandium	0.00004	73
Mercury	0.00003	73
Gold	0.000006	79
Radium	2-30 x 10 ⁻¹¹	64

^a From Sverdrup, Johnson, and Fleming, "The Oceans"

^b Normally present as sulfate but may be present as sulfide in stagnant waters or in bottom sediments due to bacterial action.

^c Almost entirely bicarbonate ion when organic matter is discounted.

^d Probably present in undissociated boric acid

^e Represents silicon present as silicate which is important in metabolism of diatoms. Lower values noted in surface layers.

^f Includes only nitrate, nitrite, and ammonia.

TABLE IX
Average Ion Abundance Ratios

<u>Ion</u>	<u>Cl-Ratio</u>	<u>Uncertainty</u>	<u>grams/liter</u>	<u>Source</u>
Cl	0.99892	0.00002	19.8401	4,90
Br	0.00340	0.00002	0.0675	4
SO ₄	0.1394	0.0002	2.7687	132
HCO ₃	0.0735	0.002	0.1460	114
F	0.00007		0.0014	135
Na	0.5556	0.0003	11.0351	117
Ca	0.02106	0.00016	0.4183	91,138
Mg	0.06695	0.00022	1.3298	138
K	0.02000	0.00020	0.3972	138
H ₃ BO ₃	0.00137	0.000006	0.0273	81,88
Sr	0.000702	0.00002	0.0139	148

TABLE X

Ion Concentrations^a

Ion	Natural ^b Ocean Water		Proposed	L & F ^b	M-C-M ^b	Synthetic Ocean Water		Std. ^c	
						Subor ^b	46Sl8 14-O-15 P-1381		
Na ⁺	10.8094	11.0347	11.0347	10.83	11.336	10.765	10.20	9.57	9.575
Mg ⁺⁺	1.3026	1.3297	1.3297	1.303	1.263	1.325	1.317	1.137	0.870
Ca ⁺⁺	0.4097	0.4184	0.4184	0.408	0.431	0.422	0.403	0.370	0.370
K ⁺	.3891	.3972	.3972	.3833	.5376	0.389	.400	0.207	.373
Str ⁺⁺	.0136	.0139	.0139	.0136	--	--	--	--	--
Cl ⁻	19.436	19.8405	19.8405	19.440	18.414	19.445	17.952	17.28	17.277
SO ₄ ⁻⁻	2.712	2.7687	2.7687	2.751	2.653	2.708	2.400	2.394	2.393
Br ⁻	0.0659	0.0675	0.0675	0.0661	0.0461	0.057	0.604	0.0423	0.043
I ⁻	.00005	.00005	--	--	--	--	--	.00428	.0043
F ⁻	.0013	.00136	.00136	.0014	--	--	--	--	--
HCO ₃ ⁻	.1431	.1460	.1460	.1428	0.1475	0.1501	--	--	--
H ₃ BO ₃	.0266	.0272	.0272	.0266	.0594	--	--	--	--
Chlorinity	19.0	19.381	19.381	19.0	19.0	19.0	17.55	16.81	16.81
Salinity	34.33	35.01	35.01						

^a Grams per liter at 20°C

^b Converted from units of gms. per kg. per liter assuming density = 1.024

^c So-called Navy Standard

TABLE XI
Cl-Ratios

Ion	Natural Ocean Water		Proposed	L & F ^a	M-G-M ^b	Synthetic Ocean Water				Std.	
						Subow	46S18	14-0-15	P-1381		
Na ⁺⁺	0.5556	0.5556	0.5556	0.557	0.583	0.5535	0.5675	0.5650	0.556	0.556	0.556
Mg ⁺⁺	0.06695	.06695	.06695	.0670	.0649	.0681	.0733	.0674	.0661	.0661	.0506
Ca ⁺⁺	0.02106	.02106	.02106	.02097	.0222	.0217	.0224	.0227	.0215	.0215	.0215
K ⁺	.0200	.0200	.0200	.0197	.0276	.0200	.0203	--	.0012	.0012	.0217
Str ⁺⁺	.0007	.0007	.0007	.0007	--	--	--	--	--	--	--
Cl ⁻	.99894	.99895	.99895	.9990	.9470	.99945	.99893	.9987	.996	.996	.9965
SO ₄ ⁻	.1394	.1394	.1394	.1413	.1364	.1392	.1337	.1388	.1392	.1392	.1392
HCO ₃ ⁻	.00735	.00735	.00735	.00683	.00758	.00782	--	--	--	--	--
Br ⁻	.00340	.00340	.00340	.00340	.00237	.00293	.0336	--	0.00246	0.00246	.00250
I ⁻	3 x 10 ⁻⁶	--	--	--	--	--	--	--	.000249	.000249	.00250
F ⁻	.00007	.00007	.00007	.000072	--	--	--	--	--	--	--
H ₃ BO ₃	.00137	.00137	.00137	.00137	.00306	--	--	--	--	--	--
Chlorinity	19.0	19.381	19.381	19.0	19.0	19.0	17.55	19.27	16.81	16.81	16.81

a Lyman and Fleming's Formula (Table VII)
b McClelland, Gault and Mulholland's Formula (Table VI)

TABLE XII

Proposed Synthetic Ocean Water

<u>Salt</u>	<u>Class I</u>	<u>Class II</u>
	<u>(gms. per liter)</u>	
NaCl	24.5336	24.54
MgCl ₂ .6H ₂ O	11.1120	11.11
Na ₂ SO ₄	4.0944	4.094
CaCl ₂	1.1587	1.159
KCl	.6945	0.695
NaHCO ₃	.2011	.201
KBr	.1005	.101
H ₃ BO ₃	.0272	.027
SrCl ₂ .6H ₂ O	.0423	.042
NaF	.0030	.003

Chlorinity 19.381
pH = 8.2 (after adjustment with 0.1 n. Na₂CO₃)

TABLE XIII

Preparation of Stock Solutions
for Proposed Synthetic Ocean Water

Stock Solution #1

MgCl ₂ .6H ₂ O	3889.2	gms.
CaCl ₂ (anhydrous)	405.55	
SrCl ₂ .6H ₂ O	14.79	

Dissolve and dilute to seven liters

Stock Solution #2

KCl	486.15	
NaHCO ₃	140.73	
KBr	70.35	
H ₃ BO ₃	19.04	
NaF	2.10	

Dissolve and dilute to seven liters

Preparation of Synthetic Ocean Water

NaCl	245.34	gms.
Na ₂ SO ₄	40.94	

Dissolve in a few liters of water

Stock Solution No. 1	200	ml.
Stock Solution No. 2	100	ml.

Dilute to ten (10) liters and adjust the pH to 8.2 with 0.1 normal Na₂CO₃. Only a few milliliters of the carbonate solution will be required if pure chemicals are used.

TABLE XIV

Heavy Metal Salts For Synthetic Ocean Water

Stock Solution No. 3

<u>Salt</u>	<u>Salt</u> <u>gms./liter</u>
$\text{Ba}(\text{NO}_3)_2$	0.994
$\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	0.546
$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$	0.396
$\text{Zn}(\text{NO}_3)_2$	0.151
$\text{Pb}(\text{NO}_3)_2$.066
AgNO_3	.0049

When heavy metals are desired, add one ml. of this stock solution to 10 liters of the synthetic ocean water prepared as directed in Table XIII. Stir vigorously with low rate of addition by means of a pipette.

TABLE XV

Corrosion Products on Zinc Alloys

Interatomic Distances

Natural Water	Synthetic Water	Basic Zinc Carbonate ^a	Basic Zinc Chloride ^b	Basic Zinc Sulfate ^c	Zinc Sulfate ^d	Zinc Hydroxide
12.2	13.0					
10.2	10.9					13.0
7.6	7.9	9.7	7.9			
6.3	6.6	6.9		6.4		6.6
5.2	5.4		5.4	5.5		
4.7	4.9					
4.41	4.44					
4.29						4.38
4.09	4.00	4.10	4.00	4.32		4.03
			3.90			
3.79	3.77					
3.70		3.69		3.68		
3.50	3.60		3.58	3.52	3.64	
				3.44		
3.32	3.29				3.30	3.27
3.22	3.20	3.18	3.17	3.18		
3.09						
	2.98	2.98				
2.89	2.90	2.88	2.92			
			2.86			
	2.73	2.74	2.71	2.72	2.71	2.71
2.68	2.70	2.69				
		2.67				
	2.60	2.60				
2.53	2.55	2.55	2.58	2.58	2.56	2.57
2.49	2.49	2.50	2.46	2.51		
2.44	2.40	2.43			2.39	2.45
2.36	2.34	2.33	2.36	2.32		2.35
						2.26
2.16	2.19	2.20		2.20	2.19	2.20
2.11	2.11	2.11	2.15	2.15		2.14
2.06	2.04	2.07	2.01	2.07		
1.97	1.98			1.98	2.02	1.964
1.92		1.93	1.948			
	1.90					1.900
1.87			1.86		1.852	1.850
1.85	1.83				1.821	
1.81	1.79	1.793	1.79	1.81		
1.77		1.773	1.763		1.761	1.740
1.69	1.71	1.708	1.682			

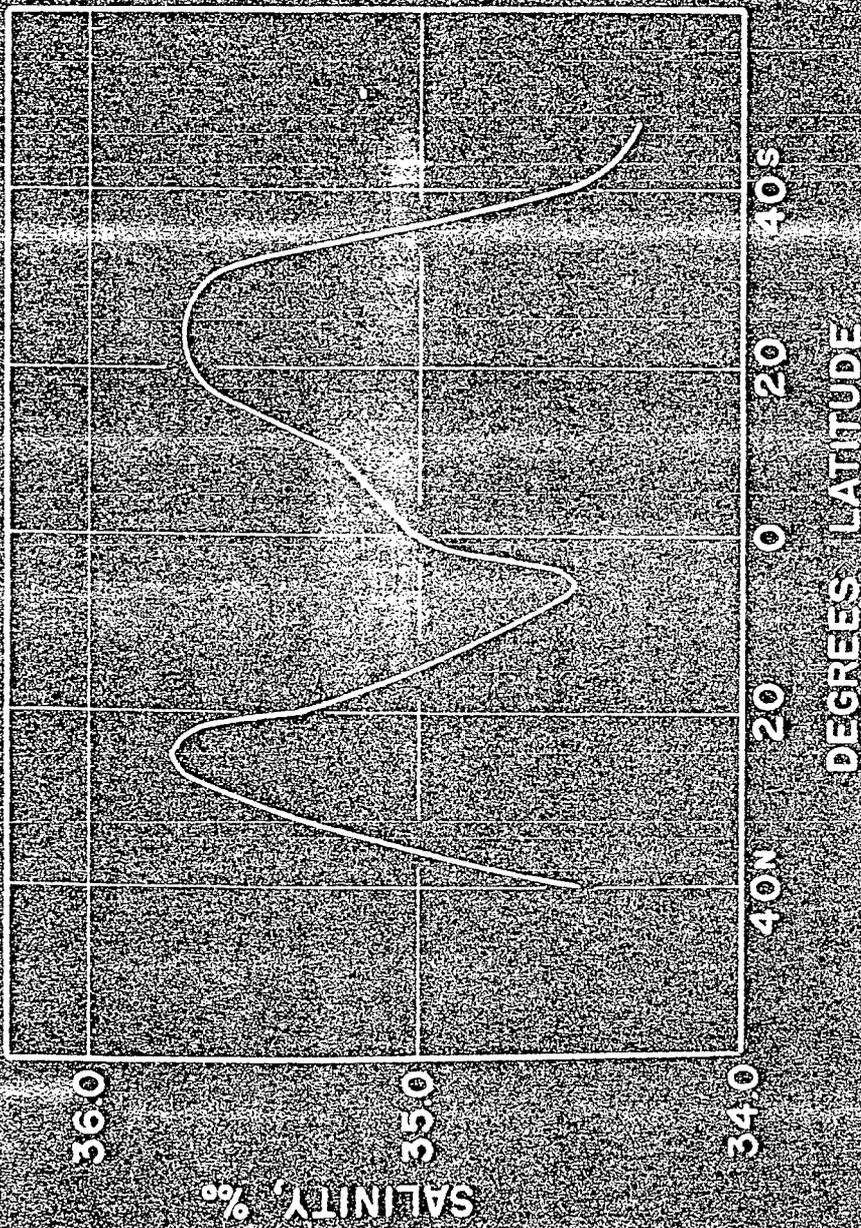
a $2ZnCO_3 \cdot 3Zn(OH)_2$ b $ZnCl_2 \cdot 4Zn(OH)_2$ c $ZnSO_4 \cdot 3Zn(OH)_2$ d $7ZnO \cdot SO_3 \cdot H_2O$

TABLE XVI

Corrosion of Low Carbon Steel at 95°F
in Spray of Sodium Chloride Solution.

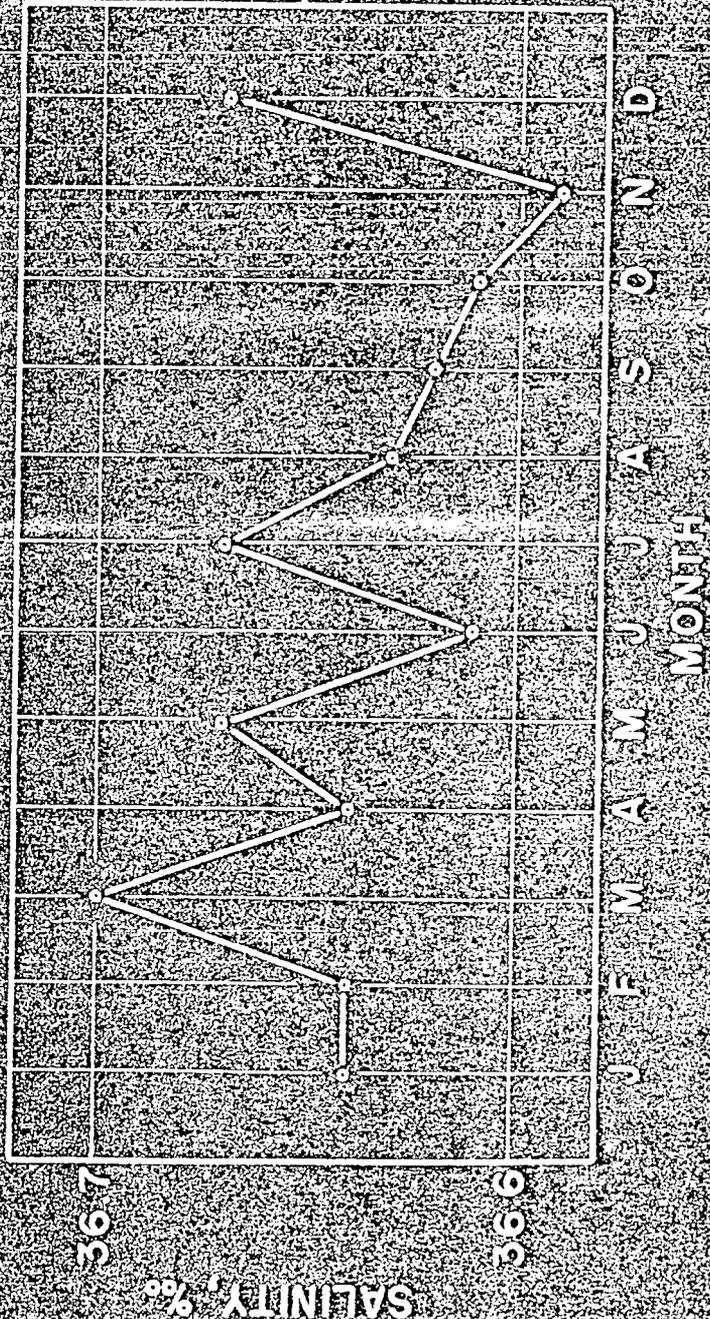
Concentration %	Corrosion Rate ^a mdd
0	0.723
0	.695
3	.622
5	.447
10	.353
15	.297
20	.271

^a Weight losses expressed in milligrams per square decimeter per day for 24-hour exposure test runs.



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FIG. 1



MID-NORTH ATLANTIC 18°N TO 42°N

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